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<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p>(21) International Application Number: PCT/EP96/05004</p> <p>(22) International Filing Date: 8 November 1996 (08.11.96)</p> <p>(30) Priority Data: P 9502188 8 November 1995 (08.11.95) ES</p> <p>(71) Applicant (for all designated States except US): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): CANOS, Avelino Corma [ES/ES]; Universidad Politécnica De Valencia, Avenida Los Naranjos, E-46071 Valencia (ES). SEGUI, Vicente Fomes [ES/ES]; Universidad Politécnica De Valencia, Avenida Los Naranjos, E-46071 Valencia (ES). PERGHER, Sibelle Berenice Castella [ES/ES]; Universidad Politécnica De Valencia, Avenida Los Naranjos, E-46071 Valencia (ES).</p> </td> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p> </td> </tr> </table>			<p>(21) International Application Number: PCT/EP96/05004</p> <p>(22) International Filing Date: 8 November 1996 (08.11.96)</p> <p>(30) Priority Data: P 9502188 8 November 1995 (08.11.95) ES</p> <p>(71) Applicant (for all designated States except US): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): CANOS, Avelino Corma [ES/ES]; Universidad Politécnica De Valencia, Avenida Los Naranjos, E-46071 Valencia (ES). SEGUI, Vicente Fomes [ES/ES]; Universidad Politécnica De Valencia, Avenida Los Naranjos, E-46071 Valencia (ES). PERGHER, Sibelle Berenice Castella [ES/ES]; Universidad Politécnica De Valencia, Avenida Los Naranjos, E-46071 Valencia (ES).</p>	<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>														
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<p>(54) Title: OXIDE MATERIALS AND CATALYST COMPOSITIONS CONTAINING THEM</p>																		
<p>(57) Abstract</p> <div style="display: flex; justify-content: space-between;"> <div style="width: 35%;"> <p>The present invention provides an oxide material having in its calcined form an X-ray diffraction pattern including values substantially as set forth in Table (I) and an adsorption capacity for 1,3,5-trimethylbenzene at a temperature of 42 °C and a pressure of 173.3 Pa (1.3 torr) of at least 0.50 mmol/g; a process for its preparation; a catalyst composition containing it; and use of the catalyst composition in a process for catalytically cracking a hydrocarbonaceous feedstock.</p> </div> <table style="width: 60%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left; padding-bottom: 10px;">d (Ångstrom)</th> <th style="text-align: left; padding-bottom: 10px;">Relative Intensity, I/I₀ x 100</th> </tr> </thead> <tbody> <tr> <td>12.49 ± 0.24</td> <td>vs</td> </tr> <tr> <td>11.19 ± 0.22</td> <td>m-s</td> </tr> <tr> <td>6.43 ± 0.12</td> <td>w</td> </tr> <tr> <td>4.98 ± 0.10</td> <td>w</td> </tr> <tr> <td>4.69 ± 0.09</td> <td>w</td> </tr> <tr> <td>3.44 ± 0.07</td> <td>vs</td> </tr> <tr> <td>3.24 ± 0.06</td> <td>w</td> </tr> </tbody> </table> </div>			d (Ångstrom)	Relative Intensity, I/I ₀ x 100	12.49 ± 0.24	vs	11.19 ± 0.22	m-s	6.43 ± 0.12	w	4.98 ± 0.10	w	4.69 ± 0.09	w	3.44 ± 0.07	vs	3.24 ± 0.06	w
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OXIDE MATERIALS AND
CATALYST COMPOSITIONS CONTAINING THEM

The present invention relates to oxide materials, a process for their preparation, catalyst compositions containing them and use of the catalyst compositions in a process for catalytically cracking a hydrocarbonaceous feedstock.

Laminar materials that swell or expand in the presence of water and/or appropriate intercalating cations are exemplified by clays, zirconium phosphates and phosphonates, hydroxycarbonates such as hydrotalcite, silicas such as kanemite, magadiite and keniaite, transition metal sulphides, graphite and laminar hydroxides. The individual layers of these materials are linked together by weak bonds such as hydrogen bonds and electrostatic forces which are easily ruptured when the intercalating force or the solvation energy of the cations exceeds the force of attraction between the layers. This is the case for example with sodium montmorillonite which swells in the presence of excess water until the distance between its layers exceeds 10 nm (100 Å). An advantage of such swellable or expandable materials, particularly those having catalytic uses, is that the space between their layers and so their internal surface can be made accessible to reactive molecules, thereby considerably increasing the catalytically active surface area of the material. However, when the intercalated cations in the swollen or expanded laminar material are eliminated by calcination, the laminar material collapses and the original spacing between the layers is re-established.

- 2 -

In order to prevent this collapse between the layers on calcination, it has been proposed in the art to intercalate in the swelled or expanded laminar material some "columns" or "pillars" of thermostable hydroxides and oxides. These columns consist of polymeric hydroxides, for example, of aluminium, silicon, chromium, nickel or zirconium. On calcination, these hydroxides give rise to columns of the corresponding oxides which are anchored in the surface of the layers, keeping them at a certain distance from one another. This stabilises the final product which is known as a "pillared laminar material". The preparation of a pillared laminar oxide material, in particular MCM-36, is described in detail in Published International Patent Application No. WO 92/11934.

It would be desirable to prepare a calcined, oxide material having an increased active surface area which is not a pillared material.

In accordance with the present invention, there is therefore provided an oxide material having in its calcined form an X-ray diffraction pattern including values substantially as set forth in Table I below:

Table I

d (Ångstrom)	Relative Intensity, I/I ₀ x 100
12.49 ± 0.24	vs
11.19 ± 0.22	m-s
6.43 ± 0.12	w
4.98 ± 0.10	w
4.69 ± 0.09	w
3.44 ± 0.07	vs
3.24 ± 0.06	w

- 7 -

treatment, e.g., at a frequency of 50 Hz and a power of 50 W for 15 minutes to 1 hour, and subsequently calcined, the product obtained is an oxide material according to the present invention.

5 Calcination may be carried out in air or an inert gas such as nitrogen at elevated temperature, e.g., at a temperature in the range from 200 to 800 °C, for a period, e.g., from 1 to 48 hours. The calcination is conveniently carried out in nitrogen gas at 540 °C for
10 5 hours.

In a preferred aspect of the invention, the present process also comprises an acid treatment step following the delamination step and prior to calcination.

15 The acid treatment step may conveniently be carried out by contacting the at least partially delaminated swollen, layered oxide material having the X-ray diffraction pattern of Table II with a strong acid, e.g. a mineral acid such as hydrochloric acid or nitric acid, at low pH, e.g. pH 2, in order to flocculate the very
20 small particles of oxide material. The oxide material thus acidified is then washed with water until a pH of 6 or more is obtained before being calcined.

In a further aspect of the invention, the present process also comprises a hydrothermal (steam) treatment
25 step and/or a fluorine/phosphorus treatment step in accordance with techniques conventional in the art. These treatments are preferably carried out post-calcination as opposed to pre-calcination.

30 The oxide material according to the present invention exhibits unique characteristics that are very different from those of zeolite MCM-22 as regards its surface area, porosity, acidity, thermal stability and catalytic behaviour.

35 Tables 1 and 2 below compare the surface areas in m²/g of calcined samples (carried out at 540 °C for

- 8 -

5 hours) of MCM-22 zeolite and the oxide material of the present invention, the latter having been prepared with (Table 2) and without (Table 1) an acid treatment from different MCM-22 precursors with silicon to aluminium atomic ratios from 15 to 100. The surface areas were determined by the well known Brunauer-Emmett-Teller (BET) method (S. Brunauer, P. Emmett and E. Teller, J. Am. Chem. Soc., 60, 309 (1938)) and the t-plot method, using nitrogen as the adsorbate.

10

Table 1
(without acid treatment)

Sample	Si/Al atomic ratio of MCM-22 precursor	Total surface area	Microporous surface area	External surface area
MCM-22	15	453	312	141
Invention	15	515	223	292
MCM-22	50	451	355	96
Invention	50	592	240	352

- 9 -

Table 2
(with acid treatment)

Sample	Si/Al atomic ratio of MCM-22 precursor	Total surface area	Microporous surface area	External surface area
MCM-22	15	453	312	141
Invention	15	637	219	418
MCM-22	25	448	339	109
Invention	25	632	150	482
MCM-22	50	451	355	96
Invention	50	841	45	796
MCM-22	100	455	379	76
Invention	100	698	150	548

The data presented in Tables 1 and 2 clearly show that delamination reduces the microporous surface area and greatly increases the external surface area compared with the values obtained for zeolite MCM-22.

5 Table 3 below shows the amount of pyridine adsorbed in mmol pyridine per gram at three different temperatures by calcined samples (carried out at 540 °C for 5 hours) of MCM-22 zeolite and the oxide material of the present invention, the latter having been prepared with or
10 without an acid treatment from two MCM-22 precursors with silicon to aluminium atomic ratios of 15 and 50. (For the adsorption coefficient, see C.A. Emeis, J. Cata., 141, 347-354 (1993).)

- 10 -

Table 3

Sample	Si/Al atomic ratio of MCM-22 precursor	Temperature (°C)					
		150		250		350	
		B	L	B	L	B	L
Invention*	15	27	11	22	9	15	9
Invention*	50	21	24	16	20	7	15
MCM-22	15	78	29	63	24	45	20
Invention#	15	72	49	51	29	33	23
MCM-22	50	39	23	24	15	15	14
Invention#	50	21	23	15	20	9	15

* denotes without acid treatment

denotes with acid treatment

B denotes Brönsted acidity

L denotes Lewis acidity

The oxide material according to the present invention may be used as a catalyst in organic conversion processes, e.g. in the catalytic cracking of hydrocarbonaceous feedstocks, and may be used alone or in combination with other catalyst components.

Accordingly, the present invention further provides a catalyst composition comprising an oxide material according to the present invention and a matrix material.

The matrix material may be an active or inactive material and may be either synthetic or naturally-occurring. Examples of matrix materials that may be employed in the catalyst composition of the invention include clays (e.g. bentonite and kaolin) and inorganic refractory oxides (e.g. silica, alumina, magnesia, titania, zirconia, silica-alumina, silica-magnesia, silica-titania, silica-zirconia, silica-thoria, silica-

- 11 -

beryllia as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia).

5 The relative proportions of the oxide material of the invention and matrix material in the catalyst composition may vary widely. Thus, for example, the catalyst composition may comprise from 0.5 to 95 %w, preferably from 1 to 80 %w of the present oxide material and from 5 to 99.5 %w, preferably from 20 to 99 %w of matrix material, all percentages by weight being calculated on 10 the basis of the combined dry weight of the present oxide material and the matrix material.

Depending on its application, the catalyst composition of the invention may further comprise at 15 least one catalytically-active metal component. Examples of catalytically-active metal components that may be used include Group VIB (e.g. molybdenum and tungsten) and Group VIII metals (e.g. cobalt, nickel, iridium, platinum and palladium), their oxides and sulphides. The catalyst composition may contain up to 50 parts by weight of 20 catalytically-active metal component, calculated as metal per 100 parts by weight of total catalyst composition. For example, the catalyst composition may contain from 2 to 40, preferably from 5 to 30, parts by weight of Group 25 VIB metal(s) and/or from 0.05 to 10, preferably from 1 to 6, parts by weight of Group VIII metal(s), calculated as metal per 100 parts by weight of total catalyst composition.

30 The catalyst composition of the invention may be prepared in accordance with techniques conventional in the art.

The present invention still further provides a process for catalytically cracking a hydrocarbonaceous feedstock which comprises contacting the feedstock at

- 12 -

elevated temperature with a catalyst composition according to the invention.

The hydrocarbonaceous feedstocks useful in the present process can vary within a wide boiling range. They include relatively light petroleum fractions such as kerosine, and heavier petroleum fractions such as vacuum distillates, long residues, deasphalted residual oils and atmospheric distillates, e.g. (vacuum) gas oils.

The present process may be carried out in a fixed catalyst bed but is preferably carried out in an upwardly or downwardly moving catalyst bed, e.g. in the manner of conventional Thermoform Catalytic Cracking (TCC) or Fluidised Catalytic Cracking (FCC) processes. The process conditions are preferably a reaction temperature in the range from 400 to 900 °C, more preferably from 450 to 800 °C and especially from 500 to 650 °C; a total pressure of from 1×10^5 to 1×10^6 Pa (1 to 10 bar), in particular from 1×10^5 to 7.5×10^5 Pa (1 to 7.5 bar); a catalyst/feedstock weight ratio (kg/kg) in the range from 0.1 to 150, especially 20 to 100 if a moving catalyst bed is used; and a contact time between catalyst and feedstock in the range from 0.1 to 100 seconds, with contact times in the range from 0.1 to 10 seconds being preferred if a moving catalyst bed is used.

The present invention will be further understood from the following illustrative examples.

Example 1

(i) Preparation of swollen, layered oxide material

A swollen, layered oxide material as described in Published International Application No. WO 92/11934 was prepared by dissolving sodium aluminate (0.233 g, 56% alumina/37% sodium oxide, from Carlo Erba) and 98% sodium hydroxide (0.810 g, from Prolabo) in deionized water (103.45 g). To this solution were added hexamethyleneimine (6.347 g, from Aldrich) and "Aerosil

- 13 -

200" (trade mark) silica (7.680 g, from Degussa) and the resulting mixture was stirred vigorously for 30 minutes. The mixture produced a gel having a silicon to aluminium atomic ratio of 50 (corresponding to a silica to alumina molar ratio of 100) which was kept in an autoclave operated at 60 rpm for 11 days at 135 °C. Centrifugation at 10,000 rpm followed by washing until the pH of the washing water became 9 or less and then drying yielded a swellable material of the type prepared in Example 1 of WO 92/11934.

A suspension of the swellable material (3 g) in a system containing bidistilled water (40 g), cetyltrimethylammonium hydroxide/bromide in a 1:1 ratio (60 g) and tetrapropylammonium hydroxide/bromide in a 1:1 ratio (18.5 g) was refluxed at 80 °C for 16 hours and then thoroughly washed with water before separation into a liquid phase and a solid phase (3.5 g). The solid phase comprised the desired swollen, layered oxide material of the type prepared in Example 2 of WO 92/11934 having an X-ray diffraction pattern substantially as shown in the Table II below.

Table II

d (Å)	Relative Intensity, $I/I_0 \times 100$
> 32.2	vs
12.41 ± 0.25	w-s
3.44 ± 0.07	w-s

- 14 -

(ii) Preparation of a calcined, oxide material according to the invention

5 Bidistilled water (600 ml) was added to the swollen, layered oxide material (3.5 g) obtained in Example 1(i) above with constant stirring and the resulting suspension was subjected to an ultrasound treatment at a frequency of 50 Hz and a power of 50 W for a period of 40 minutes. The suspension thus treated was then centrifuged, dried at 100 °C and finally calcined at 540 °C for 5 hours to
10 yield an oxide material according to the present invention (1.5 g) having an X-ray diffraction pattern as shown in Table I above and a total surface area of about 600 m²/g (of which about 350 m²/g is external surface area) as determined by the well known t-plot method using
15 nitrogen as the adsorbate.

Example 2

The process according to Example 1 above was repeated except that the amounts of reagents in step (i) were varied to produce a gel having a silicon to aluminium
20 atomic ratio of 15 (corresponding to a silica to alumina molar ratio of 30).

The calcined, oxide material obtained from step (ii) was found to have an X-ray diffraction pattern as shown in Table I above and a total surface area of over
25 500 m²/g (of which about 250 m²/g is external surface area).

Example 3

The process according to Example 2 above was repeated except that in step (i) the suspension containing the
30 swellable material of the type prepared in Example 1 of WO 92/11934, bidistilled water, cetyltrimethylammonium hydroxide/bromide and tetrapropylammonium hydroxide/bromide was heated in an autoclave at 105 °C for 42 hours.

The calcined, oxide material obtained from step (ii) was found to have an X-ray diffraction pattern as shown in Table I above and a total surface area of 400 m²/g (of which about 230 m²/g is external surface area).

5

Example 4

The process according to Example 3 above was repeated except that in step (i) the suspension containing the swellable material of the type prepared in Example 1 of WO 92/11934, bidistilled water, cetyltrimethylammonium hydroxide/bromide and tetrapropylammonium hydroxide/bromide was heated in an autoclave at 105 °C for 42 hours, washed with water and then finally with aqueous 6 N hydrochloric acid before separation into a liquid phase and a solid phase.

15

The calcined, oxide material obtained from step (ii) was found to have an X-ray diffraction pattern as shown in Table I above and a total surface area of 520 m²/g (of which about 300 m²/g is external surface area).

20

Example 5

The process according to Example 1 above was repeated except that in step (ii), following the ultrasound treatment, the suspension was lyophilised prior to calcination.

25

Example 6

The first step of the process described in Example 1 was repeated to yield a swollen, layered oxide material of the type prepared in Example 2 of WO 92/11934 having an X-ray diffraction pattern substantially as shown in the Table II above.

30

In a second step, bidistilled water (300 ml) was added to the swollen, layered oxide material (3.0 g) obtained in the first step with constant stirring and the resulting suspension was subjected to an ultrasound treatment at a frequency of 50 Hz and a power of 50 W for

35

- 16 -

a period of 1 hour. The suspension was then acidified with 6M hydrochloric acid until a pH of 2 was reached, washed with water and centrifuged several times until a pH ≥ 6 was obtained. Drying at 100 °C followed by calcination at 540 °C for 5 hours yielded an oxide material according to the present invention (2.25 g) having an X-ray diffraction pattern as shown in Table I above and a total surface area of 841 m²/g (of which 796 m²/g is external surface area).

Example 7

Cracking Experiments

A vacuum gasoil feedstock was cracked in an automated microactivity test (MAT) reactor that accomplishes standard test method ASTM D-3907 using, as cracking catalyst, 1 g of a calcined, oxide material as prepared in Example 6 above via an initial gel having a silicon to aluminium atomic ratio of 50, diluted with 2 g of a silica matrix (a catalyst according to the invention, hereinafter referred to as C_I).

For comparison, the test was repeated using, as cracking catalyst, 1 g of MCM-22 zeolite prepared as described in US-A-4 954 325 via an initial gel having a silicon to aluminium atomic ratio of 50, diluted with 2 g of the silica matrix (a comparative catalyst, hereinafter referred to as C_C).

The tests on both catalysts were carried out at different catalyst/oil weight ratios but the contact time (time on stream) remained the same. The properties of the vacuum gas oil, the process conditions used and the results obtained for each catalyst are shown in the following Tables III and IV. In Table IV, conversion is defined as the sum of the C₁-C₄ gas, gasoline (C₅ - 195 °C fraction), middle distillates (195 - 360 °C fraction) and coke yields, the yields quoted being calculated as per cent by weight on the feedstock.

- 17 -

Table III

Properties of vacuum gas oil feedstock

Density (g/cm ³ at 60 °C)	0.873
API gravity	30.68
Nitrogen content (ppm)	370
Sulphur content (%w)	1.65
Conradson Carbon (%w)	0.03
Viscosity at 50 °C (cSt)	8.249
Distillation Range (°C):	
Initial Boiling Point	167
5 %w	245
10 %w	281
20 %w	304
30 %w	328
40 %w	345
50 %w	363
60 %w	380
70 %w	401
80 %w	425
90 %w	450
Final Boiling Point	551

Table IV

Test Run	1	1A	2	2A	3	3A	4	4A	5	5A
Catalyst	CI	CC	CI	CC	CI	CC	CI	CC	CI	CC
Temp. (°C)	500	500	500	500	500	500	500	500	500	500
Catalyst/Oil (wt/wt)	0.135	0.139	0.202	0.208	0.266	0.278	0.340	0.345	0.403	0.415
Time on stream (s)	75	75	75	75	75	75	75	75	75	75
Conversion (%w)	37.94	27.38	45.20	34.53	50.45	40.78	55.31	45.54	59.51	47.30
C ₁ -C ₄ gases (%w)	8.96	7.96	12.63	11.24	15.87	14.17	18.89	16.89	21.99	20.49
Gasoline (%w)	20.21	13.87	22.91	15.84	24.18	18.01	25.37	19.03	26.20	17.96
Middle distillates (%w)	7.76	4.56	8.12	5.96	8.37	6.63	8.96	7.14	8.86	5.90
Coke (%w)	1.01	0.99	1.54	1.49	2.03	1.97	2.09	2.46	2.44	2.96

- 19 -

As the results in Table IV clearly show, the catalyst according to the invention (C_I) was significantly more active than the comparative catalyst (C_C) and produced higher gasoline and middle distillates yields with less coke formation. Indeed, the catalyst according to the invention gave a better distribution of products. Furthermore, although not shown in Table IV, the catalyst according to the invention gave a more advantageous gaseous product containing higher propylene/propane, butene/butane and isobutene/butene ratios than the gaseous product obtained using the comparative catalyst.

Example 8

The process according to Example 6 was repeated with an additional post-calcination hydrothermal treatment step carried out at 750 °C and 100% steam for 5 hours.

Example 9

Cracking Experiments

The oxide material obtained in Example 8 above (via an initial gel having a silicon to aluminium atomic ratio of 50) was formulated into a cracking catalyst according to the invention (1 g oxide material and 2 g silica matrix) and tested as previously described in Example 7 using the same vacuum gas oil feedstock at a temperature of 500 °C and a time on stream of 75 seconds. The cracking catalyst is hereinafter referred to as C_{IH}.

For comparison, the test was repeated using a similar cracking catalyst containing instead of the oxide material of Example 8, 1 g of MCM-22 zeolite prepared as described in US-A-4 954 325 via an initial gel having a silicon to aluminium atomic ratio of 50 which had likewise been subjected to a hydrothermal treatment step at 750 °C and 100% steam for 5 hours. The comparative cracking catalyst is hereinafter referred to as C_{CH}.

The catalyst/oil weight ratios used and the results obtained for each catalyst are shown in the following

- 20 -

5 Table V, in which conversion is defined as the sum of the C₁-C₄ gas, gasoline, middle distillates and coke yields, the yields quoted being calculated as per cent by weight on the feedstock. As will be observed from Table V the catalyst according to the invention (C_{IH}) shows improved activity relative to the comparative catalyst (C_{CH}) and produces considerably less coke.

Table V

Test Run	6	7	7A	8	8A	9	9A	10	10A
Catalyst	CIH	CIH	CCH	CIH	CCH	CIH	CCH	CIH	CCH
Catalyst/Oil (wt/wt)	0.138	0.210	0.211	0.285	0.280	0.355	0.352	0.421	0.421
Conversion (%w)	25.70	29.86	28.16	32.46	31.85	34.97	34.41	38.08	37.51
C1-C4 gases (%w)	2.63	3.89	4.08	4.94	5.08	5.84	6.20	6.59	7.07
Gasoline (%w)	13.91	15.77	15.99	16.49	17.43	17.57	18.77	18.38	19.27
Middle distillates (%w)	8.69	9.49	7.05	10.15	8.06	10.54	9.02	11.84	9.62
Coke (%w)	0.47	0.71	1.04	0.88	1.28	1.02	1.42	1.27	1.55

Example 10

The process according to Example 1 was repeated with additional post-calcination phosphorus and hydrothermal treatment steps. Thus, the calcined, oxide material obtained was contacted with a solution of ammonium dihydrogenphosphate, $(\text{NH}_4)\text{H}_2\text{P}_0_4$, in deionized water to add 2 %w phosphorus. The material so treated was dried in a rotary vacuum evaporator at 80 °C and then subjected to a hydrothermal treatment at 750 °C and 100% steam for 5 hours.

Example 11Cracking Experiments

The phosphorus-containing oxide material obtained in Example 10 above was formulated into a cracking catalyst according to the invention (1 g oxide material and 2 g silica matrix) and tested as previously described in Example 7 using the same vacuum gas oil feedstock at a temperature of 500 °C and a time on stream of 75 seconds.

The catalyst/oil weight ratios used and the results obtained are shown in the following Table VI, in which conversion is defined as the sum of the C_1 - C_4 gas, gasoline, middle distillates and coke yields, the yields quoted being calculated as per cent by weight on the feedstock.

- 23 -

Table VI

Test Run	11	12	13	14	15
Catalyst/Oil (wt/wt)	0.140	0.209	0.280	0.350	0.421
Conversion (%w)	22.51	27.94	32.14	35.46	38.64
C ₁ -C ₄ gases (%w)	2.91	3.96	5.25	6.45	7.41
Gasoline (%w)	13.08	15.57	17.39	18.44	19.93
Middle distillates (%w)	5.98	7.57	8.29	8.95	9.57
Coke (%w)	0.59	0.84	1.21	1.62	1.73

C L A I M S

1. An oxide material having in its calcined form an X-ray diffraction pattern including values substantially as set forth in Table I below:

Table I

d (Ångstrom)	Relative Intensity, I/I ₀ x 100
12.49 ± 0.24	vs
11.19 ± 0.22	m-s
6.43 ± 0.12	w
4.98 ± 0.10	w
4.69 ± 0.09	w
3.44 ± 0.07	vs
3.24 ± 0.06	w

5 and an adsorption capacity for 1,3,5-trimethylbenzene at a temperature of 42 °C and a pressure of 173.3 Pa (1.3 torr) of least 0.50 mmol/g.

2. An oxide material according to claim 1 comprising the oxides XO₂ and Y₂O₃ wherein X represents a tetravalent element and Y represents a trivalent element, the atomic
10 ratio X to Y being at least 10.

3. An oxide material according to claim 2, wherein X represents at least one tetravalent element selected from silicon and germanium.

4. An oxide material according to claim 2 or claim 3,
15 wherein Y represents at least one trivalent element selected from aluminium, boron, iron, chromium and gallium.

- 25 -

5. An oxide material according to any one of claims 2 to 4, wherein X represents silicon and Y represents aluminium.
- 5 6. An oxide material according to any one of claims 2 to 5, wherein the atomic ratio X to Y is in the range from 10 to 500.
7. An oxide material according to any one of claims 2 to 6, wherein the atomic ratio X to Y is in the range from 10 to 350.
- 10 8. An oxide material according to any one of claims 2 to 7, wherein the atomic ratio X to Y is in the range from 10 to 150.
9. A process for the preparation of an oxide material as defined in any one of the preceding claims, which
15 comprises, prior to calcination, at least partially delaminating a swollen, layered oxide material having an X-ray diffraction pattern including values substantially as set forth in Table II below:

Table II

d (Ångstrom)	Relative Intensity, I/I ₀ x 100
> 32.2	vs
12.41 ± 0.25	w-s
3.44 ± 0.07	w-s

10. A process according to claim 9, wherein the swollen, layered oxide material is at least partially delaminated using ultrasound techniques.
- 20 11. A process according to claim 9 or 10, which also comprises an acid treatment step after the delamination step.

12. A process according to any one of claims 9 to 11, which also comprises a post-calcination hydrothermal treatment step.
13. A process according to any one of claims 9 to 12, which also comprises a post-calcination fluorine and/or phosphorus treatment step.
14. An oxide material obtainable by a process as claimed in any one of claims 9 to 13.
15. A catalyst composition comprising an oxide material as defined in any one of claims 1 to 8 and 14, and a matrix material.
16. A catalyst composition according to claim 15, wherein the matrix material is a refractory oxide.
17. A process for catalytically cracking a hydrocarbonaceous feedstock which comprises contacting the feedstock at elevated temperature with a catalyst composition according to claim 15 or claim 16.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 96/05004

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B33/38 C01B39/48 B01J29/04 C10G11/04 C10G11/05

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C01B B01J C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	see claims 1-6	17
X	US 5 264 643 A (DIGUISEPPI FRANK T ET AL) 23 November 1993	1-8, 14-16
Y	see table 1	17
Y	WO 92 11934 A (MOBIL OIL CORP) 23 July 1992	17
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Inter: Application No
PCT/EP 96/05004

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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